SYNTHESIS AND CHARACTERIZATION OF POLYMER- FERROELECTRIC COMPOSITE

A dissertation submitted in partial fulfillment

FOR THE DEGREE OF MASTER OF SCIENCE IN PHYSICS

Under the Academic Autonomy

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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May 2012

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ROURKELA

CERTIFICATE

This is to certify that the thesis entitled , "**Synthesis and Characterization of Polymer-Ferroelectric composite**" submitted by **Miss Rosalin Beura** in the part of fulfillment for the requirement for the award of Master of Science Degree in Physics department at National Institute of Technology , Rourkela is an authentic work carried out by her under my supervision and guidance .

To the best of my knowledge the matter embodied in this project has not been submitted by any other university /Institute for the degree.

Rourkela

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Declaration of the candidate

I hereby declare that the project work entitled **"Synthesis and characterization of Polymer-Ferromagnetic composite"** is an authentic work carried by me, during the one year project at NIT, Rourkela, form July 2011-May2012 under the supervision of Prof.Simanchal Panigrahi and is being submitted by for the partial fulfillment of the requirement for award of degree of Master of Science in physics to NIT, Rourkela .This has not been submitted anywhere else for the award of any other degree.

Date: **Rosalin Beura**

ACKNOWLEDGEMENT

Before presenting my work I would first like to thank all those people who have been very kind enough to extend their helping hand in completing this project work.

First of all I would thank the institute for giving me an opportunity to be a part of it where I could gain knowledge and a lot of experience in the field of physics.

I extend my sincere thanks to my guide Prof. Simanchal Panigrahi for initiating me to this field of work. It was a great opportunity to work under his guidance throughout this 1 yr. His vast knowledge source helped me in enriching my knowledge power.

I thank Dr.Siddharth Jena , Professor and Head of the department for his help at various necessary steps.

I thank Dr.Tanmaya Badapanda for guiding me to do this project and helping me at certain steps while doing my project .

I owe my heartfelt gratitude to PhD. Scholar V.Senthil for his all-time support and guidance at each and every step of my project work. Without his help it would have been very difficult to complete the work. His deep and clear knowledge in this filed proved to be very fruitful. Thank You sir for the support and help.

I extend my sincere thanks to research scholar Rakesh sir, Priyambada Didi, Jashashree didi and other Ph.D scholars for their unhesitating help.

I thank the Department of ceramic engineering & Department of Metallurgical and Material science for providing all facilities to carry out XRD and SEM.

I thank all my dear classmates for their help and support at various steps.

Last but not the least I express my gratefulness to my parents without whose blessings and moral support the journey would have become very difficult.

Rosalin Beura

ABSTRACT

Materials existing in nature can be generally classified into four basic categories i.e. metals, plastics, ceramics, composites. Composites are generally materials made by the combination of two or more materials each having different physical and chemical properties. Polymer ferroelectric composite is a composite of polymer and added ferroelectric ceramic. Ferroelectric materials have a wide range of application because of its high dielectric permittivity. But it has poor mechanical strength and lower break down strength, which can be compensated by the polymer which is the matrix. In addition their properties can be tuned for the requirement by changing the properties of the constituents. Because this is an upcoming field much work is needed to understand the behavior thoroughly so that can be effectively used for various applications.

Here we prepare the composite of the polymer polyvinyl alcohol (PVA) with the ferroelectric ceramic $BaZr_{0.1}Ti_{0.9}O_3$. BZT powder were prepared by solid state reaction route and preliminary X-ray analysis for $BaZr_{0.1}Ti_{0.9}O_3$ was done which resulted the formation of single phase compound in cubic crystal system .Then the polymer composite of ferroelectric compound was prepared using polyvinyl alcohol as the polymer matrix. The SEM micrograph shows that the BZT particle distribution is homogenous with no porous matrix .The detailed study of dielectric and impedance properties of the material in a wide range of temperature ($50\text{-}150^0C$) and frequency ($10^2\text{-}10^6Hz$) showed that these properties are highly temperature and frequency dependent.

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CHAPTER -1

1. INTRODUCTION

1.1. Dielectric & Insulators

The word dielectric is derived from the prefix dia, originally means through or across. Thus dielectric is referred to as material that permits the passage of the electric field. Unlike semiconductors, the energy gap is little higher so that thermally generated charge carriers are generally absent. So at room temperature this material behaves as an insulator. In the presence of electric field charge does not flow through the dielectric material as in a conductor but only slightly shift from their average equilibrium positions causes polarization. The charge centre shifts according to the fields causes various type of polarization such as 1-electronic polarization, 2- ionic polarization, 3- orientational/dipolar polarization, and 4- space charge polarization. This polarization gives a very attractive property which is characterized by dielectric constant. When subjected to external mechanical stress, thermal variation various dielectric phenomena such as piezoelectricity, pyroelectricity and ferroelectricity appeared which are exploited for various applications in capacitors, actuators, transducers, sensors memory applications etc.

An insulator also called as dielectric is a material that resists the flow of electric charge. Here valence electron are tightly bonded to their atoms .Dielectric materials with high dielectric constants are considered insulator.

The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy in materials .This explains various phenomena in electronics, optics & solid state physics. Dielectric are used to store the electric charges while insulators are used to block the flow of electric charges .All dielectric are insulators but all insulators are not dielectric because they can't store charges like dielectric .

1.2. Piezoelectricity

Piezoelectricity is the property of charge separation in certain material in response to the applied mechanical stress. As a result a voltage developed across the surface of the material. This effect is understood as the linear electrochemical interaction between

mechanical and electrical state in crystal material with no inversion of symmetry. This is termed as direct piezoelectric effect. The piezoelectric effect is a reversible process in i.e. when the material is subjected to any external voltage, the material get strained. This is known as reverse piezoelectric effect. The materials possessing non-centro symmetric structure are come under the class of piezoelectric materials.

P=dF (direct effect)

P=Polarization

F=Stress

d =piezoelectric coefficient

For converse effect

S=dE

S=Strain

E=Electric field

Piezoelectric properties are dependent on the orientation direction, so they must be described in terms of tensor

$P_i=\Sigma\, d_{ij}\, F_j$ (direct effect)

$S_j=\Sigma\, d_{ji}\, E_i$ (i=1,2,3 j=1,2,3,4,5,6)

(indirect piezoelectric effect)

Piezoelectric effect have so many application like they can be used as transducer, actuator, sensor.

1.3. Pyroelectricity

Some crystals with non centro-symmetric structure having unique polar axis are characterized by spontaneous polarization. When such types of material are subjected to thermal treatment, the dipoles align accordingly. This property is referred as pyroelectricity.

There are 10 pyroelectric crystal classes among 21 non–centro symmetric crystal groups.

Pyroelectricity is the ability of certain materials to generate a temporary voltage when they are cooled or heated. The change in the temperature modifies the position of atoms slightly within the crystal structure such that the polarization of the material changes.

$$\Delta P_s = \Pi \Delta T$$

ΔP_s=spontaneous polarization

Π=Pyroelectric coeffectient

ΔT=change in temperature

This shows that spontaneous polarization depends upon temperature.

1.4. Ferro electricity

It is the property of certain materials characterized by a spontaneous electric polarization which can be reversed with the application of external electric field. The non centro symmetric nature of structural unit is the basic necessity for creating spontaneous polarization. The reversibility of spontaneous polarization with applied field gives a hysteresis loop which is analogous to ferromagnetism and is responsible for such naming. Ferrroelectricity[6] was discovered in 1920 in Rochelle salt (Potassium sodium tartaret, $KNaC_4H_4O_6.H_2O$) by Valasek. Thus the prefix ferro meaning iron was used to describe the property despite the fact that ferroelectric materials do not contain iron .The crystal exhibiting ferroelectricity are called ferroelectric crystal.

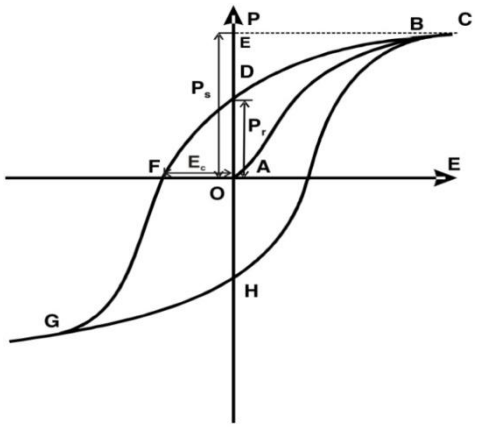


Figure 1 Ferroelectric hysteresis

The most distinctive characteristic of ferroelectricity is the hysteresis loop i.e. polarization versus electric field curve. A net spontaneous polarization exists even at zero electric field and the loop disappears at the Curie temp Tc where the material undergoes phase transition from high temperature par electric state to low temperature ferroelectric state. All ferroelectric materials have a transition temperature called Curie point (T_c) above which the crystal does not exhibits ferroelectricity and below it is ferroelectric .For more than one ferroelectric phase the temperature at which the crystal transforms from one ferroelectric phase to another is called the transition temperature.

This temperature dependence of dielectric above curie point in ferroelectric crystal is governed by the Curie –Weiss law = $\frac{C}{(T - T_C)}$

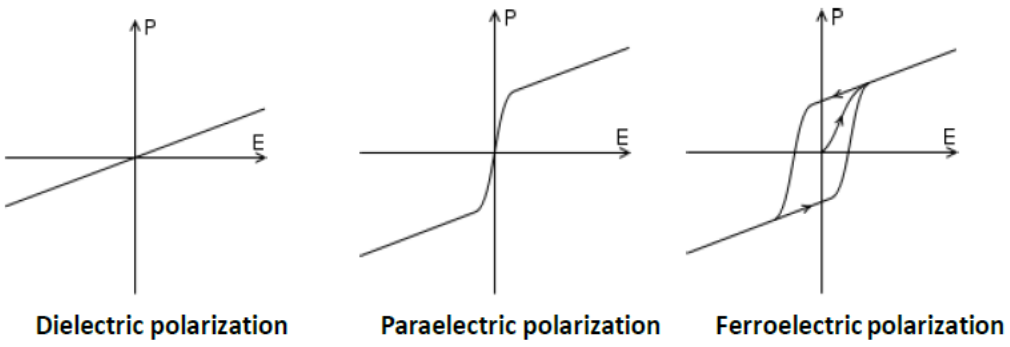


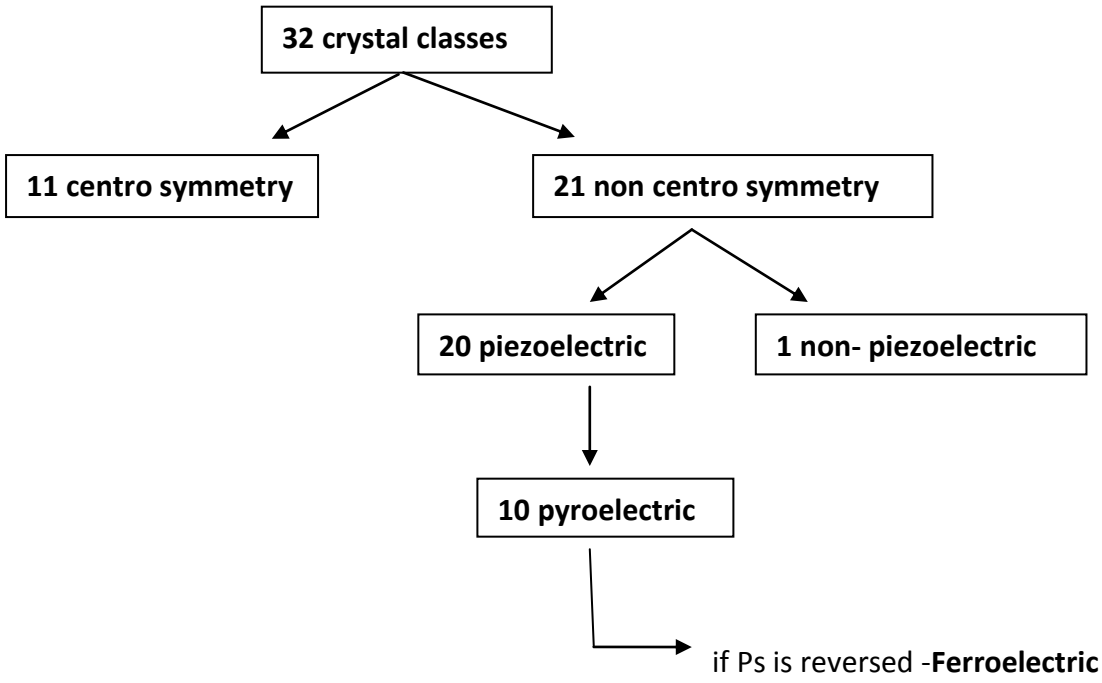
Fig-2 Various types of polarization

1.5. Basics of ferroelectric in Crystal

Solid material can be described as:

1. **Amorphous**-The atoms are arranged in random way similar to the disorder we find in liquid.eg –glass

2. **Crystalline** –The atoms are arrange in a regular pattern with a smallest volume element called unit cell that is repeated in 3D to describe the crystal.



Ferroelectric structures are of four types:

1. Perovskite structure

2. Bismuth layer structure

3. Tungsten Bronze structure

4. Pyrochlore structure

1.6. Pervoskite Structure

Any material with the same crystal structure as calcium titanium oxide ($CaTiO_3$) known as perovskite structure. Perovskite take their name from this compound which was first discovered in Ural mountain of Russia & is named after the mineralogist L.A.Perovskite .

The general Perovskite formula is ABX_3 , where 'A' & 'B' are two cations of different sizes and 'X' is an anion that bonds with the both .The 'A' atom is larger in size than the 'B' atoms. Pervokite structure is adopted by many oxides that have the chemical formula

(ABO_3). In ideal cubic unit cell of such a compound type 'A'atoms sits at cube corner positions (0, 0, 0) type 'B' atoms sits at center position (1/2,1/2,1/2) and oxygen atom sits at face centered position ,(1/2,1/2,0).

B atoms have higher charge than A atom (B:Ti^{4+},Zr^{4+},Sn^{4+},Nd^{5+},Ta^{5+},W^{6+} etc, A:Na^{+},K^{+},Ca^{2+},Ba^{2+},Pb^{2+} etc).

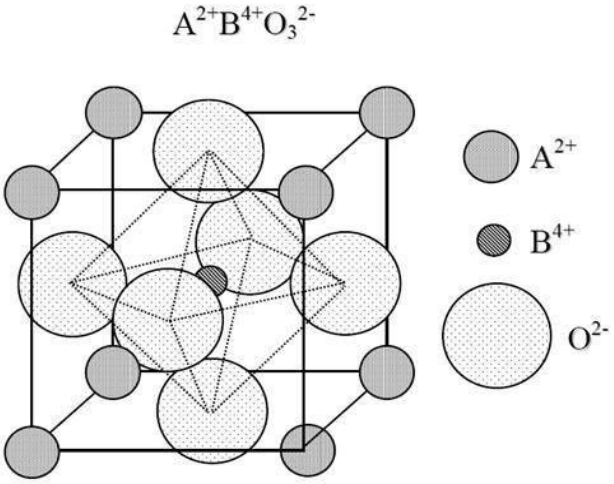


Fig.3 A cubic ABO_3, perovskite type unit cell

Barium Titanate ($BaTiO_3$)

Barium Titanate is one of the most used ferroelectric in the electronic industry finding extensive applications as dielectric material in multilayer ceramic capacitors (MLCCs), piezoelectric actuator, embedded capacitance in printed circuit boards, positive temperature coefficient of resistivity sensors. $BaTiO_3$ is an inorganic compound and a ferroelectric ceramic.

One of theBaTiO3 solid solution, $BaZ_xTi_{1-x}O_3$ [8] is one of the most important composition used as dielectric in MLCCs. The presence of Zr in $BaTiO_3$ unit cell results in a strong increase in permittivity.

At the same time the temperature characteristic is smoothened due to the broadening of the permittivity temperature dependence .The dielectric data of $BaZr_xTi_{1-x}O_3$ (BZT) ceramic suggest that

a normal ferroelectric behaviour for $0<x<0.1$

diffused phase transition $0.1<x<0.2$

relaxor characteristic $0.2<x<0.5$

The degree of diffuses of the ferro –para phase transition increases with Zr addition .For $x>0.5$ it is no more ferroelectric.

Recently discovered piezoelectric system based BZT is an addition to the potential for lead free materials .The composition lying near the morphotropic phase boundary offers comparable piezoelectric properties to other high performance lead based system.

1.7. PVA (Polyvinyl alcohol)

PVA [1,4,5] is water soluble non toxic & odorless synthetic polymer. It is made using vinyl acetate monomer by subjecting it to polymerization and partial hydrolysis. Usually prepared by dissolving it in water & letting the water evaporate to form transparent film with exceptional strength and resistance to tearing. Its solubility depends upon its degree of hydrolysis molecular wt. and tendency to hydrogen bond. It dissolves only in hot water. It has excellent adhesive property, inheritantly resistant to organic solvent, oil and grease .Its density ranges from 1.19to 1.31g/cm^3.In large amount it can be dangerous to environment ,especially if its mixed with H_2O & comes in contact with fish .It is non toxic as long as it is not burned or melted with fire. The advantages of PVA such as high mechanical strength, and water soluble has played as a main role for this selection as compared to other polymer matrices[3].

1.8. Polymer-Ferroelectric Composite

Materials are broadly classified into four main categories i.e. metals, plastics, ceramics and composites. Composites are generally artificial or naturally occurring materials that are made from the combination of two or more constituents having different physical and chemical properties. The composite materials are heterogeneous in nature.

None of materials existing in nature have all the properties that are required for various purposes. So in order to meet the demand for the required material the composite of

materials is prepared. Fabrication of composite material is nothing but the combination of two or more different material properties that often cannot be in single phase material.

Polymer composite [2] is composite made from polymer along with other kinds of material.

Polymer + ceramic = Polymer composite

Polymer has some merits like good mechanical property, easy to synthesize, low acoustic impedance and high dielectric breakdown strength and demerit is low dielectric constant. Similarly ceramic have poor mechanical properties, highly brittle, acoustic impedance and high dielectric constant and lower breakdown strength.

In order to achieve such an objective high dielectric constant ferroelectric ceramic such as BT, PZT, BZT, etc have been used as filler in polymer. These materials possess superior physical properties such as enhanced mechanical strength & improved electric properties.

1.9. Motivation

Dielectric materials with high dielectric constants are required for the reduction in the dimension of electric devices and in particular in wireless communication product such as cellular telephone & most important application is used for stress relief in high voltage electrical supply .Dielectric materials have employed throughout the electrical industry as insulators and capacitors .The properties of packaging materials significantly influence the performance of high speed microelectronic devices. Electrical characteristic such as signal attenuation, propagation velocity etc are influenced by dielectric properties of the package substrate. Materials having low dielectric constant minimize capacitance coupling and reduce signal delay. Materials with low dielectric loss reduces signal attenuation .Optimization of both properties is critical to provide superior high frequency device performance.[23]

In the recent years the need for efficient transient energy storage has motivated research for better material capable of accumulating large amount of charge per unit volume when compared to state of the art technology .The energy density is governed by its dielectric strength and permittivity. So either a new high permittivity polymer chemistry has to be developed or composite approach has to be better understand or adopted. Recent investigation

indicates these polymer ceramic material may improve only permittivity at the expense of the breakdown strength.[15-19]

Polymer[11] based microelectronic encapsulation materials are generally comprised of micron scale inorganic particulate mixed with thermosetting polymer matrix. Claussius & Mossotti performed some of the earliest work in the dielectric properties of composite materials .They have derived individually a mean field theory for the disorder system of polarizing sphere .Vo and Shi described the theoretical model to describe the effect of this interphase region on the bulk dielectric constant of polymer composite material.

Polymer composite with high dielectric constant have attracted much attention because of their flexibility and their ability to be easily fabricated into various shapes. Polythene has high dielectric very less electrical conductivity and is a kind of outstanding insulation for wires and cable application .But however its use is restricted for electrical stress control in cable termination .PVA is a water soluble nontoxic polymer. The advantages of PVA such as high mechanical strength ,and water soluble has played as a main role for this selection as compared to other polymer matrices .the polymer phase lower the density and permittivity and increase the elastic compliance of the composite .

The rapid advancement in electronic device need for a ceramic with tunable dielectric constant & low loss at microwave frequency .Ferroelectric material possess significant texability i.e change of dielectric constant on application of electric field. One of theBaTiO3 solid solution, $BaZ_xTi_{1-x}O_3$ is one of the most important compositions used as dielectric in MLCCs. The presence of Zr in $BaTiO_3$ unit cell results in a strong increase in permittivity. Hence we make a composite of BZT and PVA and study its characteristic.

Objective

- To synthesis the ferroelectric material $BaZr_{0.1}Ti_{0.9}O_3$ by solid state method
- To synthesis the polymer composite of the synthesized ferroelectric material with Poly Vinyl Alcohol
- To characterize the polymer composite by SEM for surface morphology, dielectric study for electrical properties.

CHAPTER 2

2. Experimental technique

In this chapter detailed study of synthesis of the ceramic ferroelectric ($BaZr_{0.1}Ti_{0.9}O_3$) powder, polymer composite ferroelectric materials and the experimental techniques employed to characterize the specimen are briefly discussed.

2.1. Different experimental Techniques

1. Ball mill

A ball mill[7] , a type of grinder is a cylindrical device used to grind materials into extremely fine powders for the use in mineral dressing processes, paints ,pyrotechnics& ceramics .It rotates around a horizontal axis partially filled with the material to be ground plus grinding medium (here acetone).Different materials are used as media like ceramic balls ,filth pebbles & stainless steel balls(here zirconium balls).An internal cascading effect reduces the material to fine powder .One more type of ball milling is planetary ball mill which are smaller ones and are generally used for grinding sample to smaller size in laboratories. It consists of one jar arranged eccentrically at the center of the so called sun wheel. The difference in speed between the balls and grinding jars produce an interaction between frictional and impact force with release of high dynamic energies. The interaction between these forces produces the high & very effective degree of size reduction of planetary ball mill.

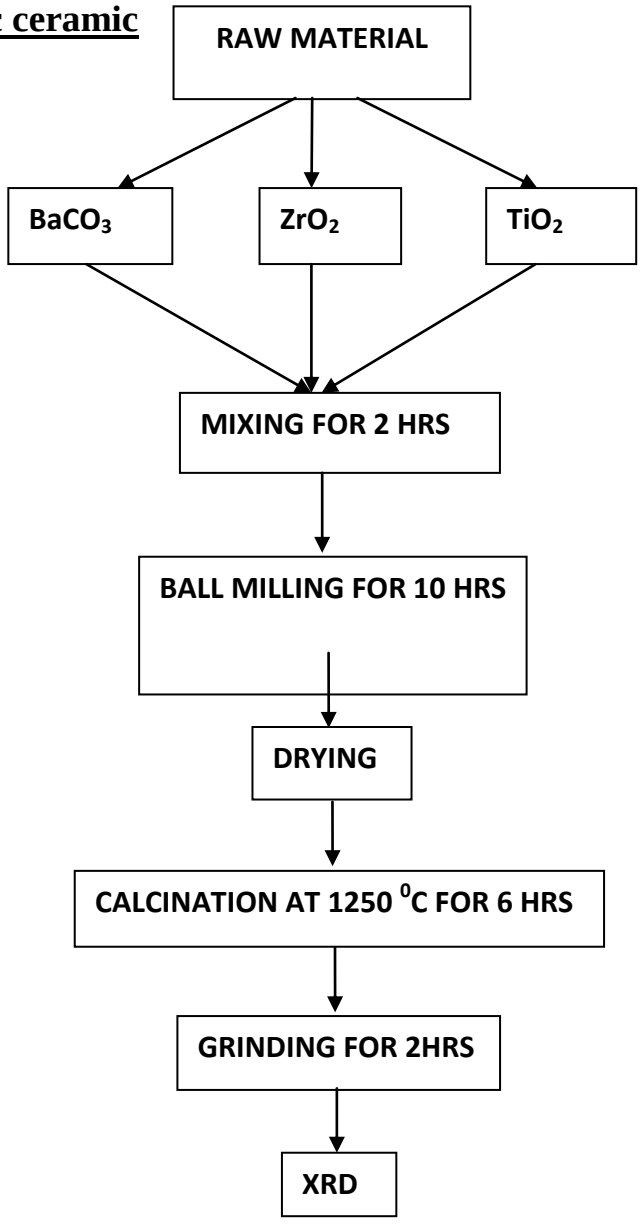
2. Calcination

Calcination is a thermal process applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or removal of a volatile fraction .Calcination normally takes place at temperature below m.p of the product material .Calcination is to be distinguished from roasting in which more complex gas –solid reaction takes place between furnace atmosphere & the solid. During calcinations intra diffusion of ions of the constituents takes place .Greater is the calcinations temperature greater is the homogeneity of the final product.

3. Hot press

Most of the times it is not possible to obtain a low porosity body by pressure less sintering i.e.by sintering in atmospheric pressure .It may prove difficult to combine the complete elimination of porosity with the maintenance of small crystal size .These problems are usually overcome by hot pressing i.e. by sintering under pressure between punches in a die . The pressure provides the major part of driving force eliminating porosity & temperature can be kept at a level at which crystal growth is minimized.

Synthesis of ferroelectric ceramic



FLOW CHART FOR SYNTHESIS OF BZT

The BZT ceramic was prepared by solid state reaction method by taking high purity raw materials such as i)Barium Carbonate ($BaCO_3$)

ii)Zirconium dioxide (ZrO_2)

iii)Titanium dioxide (TiO_2)

The constituents of the required specimen were taken in stoichiometric ratio .Mixing is accomplished by using agate mortar & pestle .Then the ceramic were ball milled for 10 hrs for proper mixing of powder in acetone medium with zirconium balls .After drying the mixed powder were kept in programmable furnace for 6 hrs followed by grinding for phase formation & removal of volatile fraction.

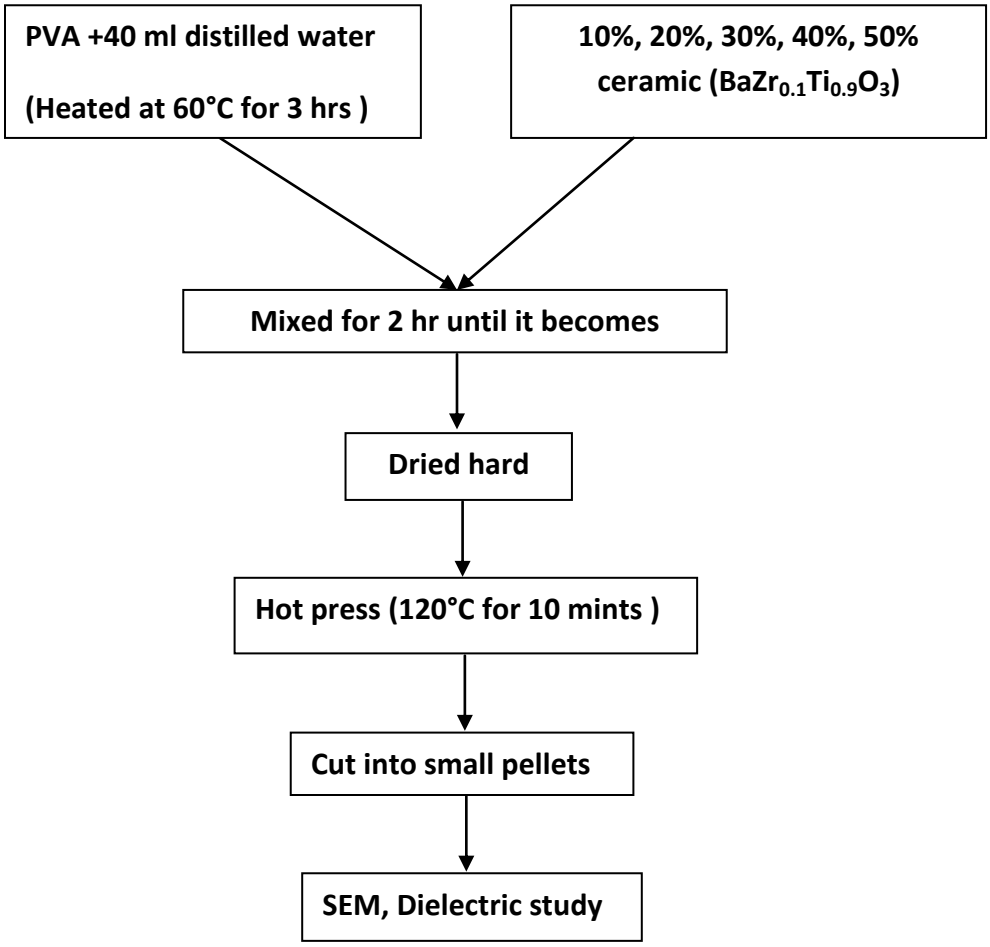
2.2. Synthesis of polymer composite (PVA-$BaZr_{0.1}Ti_{0.9}O_3$)

Density of PVA is 1.31g/cm^3 and density of $BaTiO_3$ – 6.01g/cm^3.Ceramic i.e. BZT was added to the polymer (PVA) by volume percentage i.e. 10%, 20%, 30%, 40%, 50%. Calculation was done for 1% $BaTiO_3$.Since the Zirconium percentage was very less so the composite was prepared with barium titanate.

1% $BaTiO_3$=6.01/100=0.0601g

Hence accordingly for 10%, 20%, 30%, 40%, 50% it was calculated to be 0.601g, 1.201g, 1.803g, 2.404g, and 3.005g respectively.

For preparation of polymer composite (PVA-BZT) in ratio 90/10, 1.31g of PVA & 0.601g of ceramic were taken .Then 1.3g of PVA was added to 40ml distilled water and stirred constantly at 60°C for 3 hrs by using magnetic stirrer .Then 0.601g of BZT was added to PVA suspension and mixed by agate mortar for 1 hr .After drying off the sample ,for fabrication the composite was hot pressed at 120 °C for 10 mints with a pressure of 6 tons. Then prepared PVA – $BaZr_{0.1}Ti_{0.9}O_3$composite was kept for SEM & electrical study .For electrical study silver paste was used for the electrode on both side of the samples. Similar procedure was repeated for 20%, 30%, 40%, 50% ceramic composite.



FLOW CHART FOR SYNTHESIS OF BZT

2.3. Characterization Techniques

The following techniques were characterization used to study the structural, morphological and electric study of the ceramic.

1. X-Ray diffraction

X Rays[9,25] are electromagnetic radiation of exactly the same nature of the visible light but having wavelength 10 -80cm .The X Rays used for diffraction have the wavelength lying between 0.5 -2.5 A^0 .We know that the physical properties of solid i.e. optical , electrical , magnetic ferroelectric etc. depends on atomic arrangement of materials . So X ray powder diffraction is a rapid analytical technique used for phase identification of a crystalline material & can provide information on a unit cell dimension.

Max van Laue in 1912 discovered that crystalline substances act 3-dimensional diffraction grating for x-ray wavelength similar to the spacing of planes in a crystal lattice .Hence was used determination of material & the finger print characterization of materials.

XRD is based on constructive interference of the monochromatic x-ray & crystalline sample when the condition satisfies Bragg's law

$$n\ \lambda = 2d \sin\theta$$

Where, d= spacing between atomic planes, λ = x ray wavelength, θ = angle of diffraction

n = 1, 2, 3, ……..

The diffracted x-rays are then detected, processed & counted .By scanning the sample through a range of 2θ angle all possible diffraction direction of the lattice should be attained due to random orientation of powder crystal. Conversion of diffraction peak to d-spacing allows identification of a mineral because mineral has a set of unique d – spacing.

2. **Scanning electron microscopy (SEM)**

A scanning electron microscope is a type of electron microscope that images a sample by scanning it with a beam of electron in a raster scan pattern .In SEM when a beam of highly energetic electron strikes the sample the secondary electron, back scattered, are ejected from the sample .The electron interact with the atoms that make up the sample producing signals that are collected at the detector. These signals contain information about the samples surface topography, composition & other properties such as electrical conductivity.

3. **Dielectric Measurement**

To measure the relative permittivity (dielectric constant) and dielectric loss, LCR meter can be used to measure the dielectric constant and dielectric loss. The electrode samples were used to make the measurements. The LCR meter, was connected with the computer and the data was collected as a function of temperature at different frequencies. The following formula was used to calculate the dielectric constant

$$C = \frac{\varepsilon_r A}{d}$$

C= Capacitance in faraday (F), ε = Permittivity of free space in farad per meter (8.85 x 10-12F/m), ε_r = Dielectric constant or relative permittivity of the sample, A= Area of each plane electrode in square meters (m^2) ,d = Separation between the electrodes in meters (m)

4. Impedance spectroscopy

Dielectric spectroscopy also known as electrochemical impedance spectroscopy measures the dielectric properties of a medium as function of frequency .It is based on the interaction of the external field with the electric dipole moment of the sample .Impedance is the opposite to the flow of system comprises both energy dissipate & energy storage element . Impedance is the opposition to the flow of AC in a complex system .A passive complex electrical system comprises both of energy dissipated & storage element. It is a powerful tool to investigate the electrical properties of the complex perovskite oxides. The main advantages of the techniques, i) it involves relatively simple electrical measurements that can readily be automated ii) the measurements can be implemented by using arbitrary electrodes iii) the results can be often correlated with the properties such as composition, microstructure, defects, dielectric properties, chemical reaction etc. of the sample.

CHAPTER 3

Result and Discussion

1. XRD

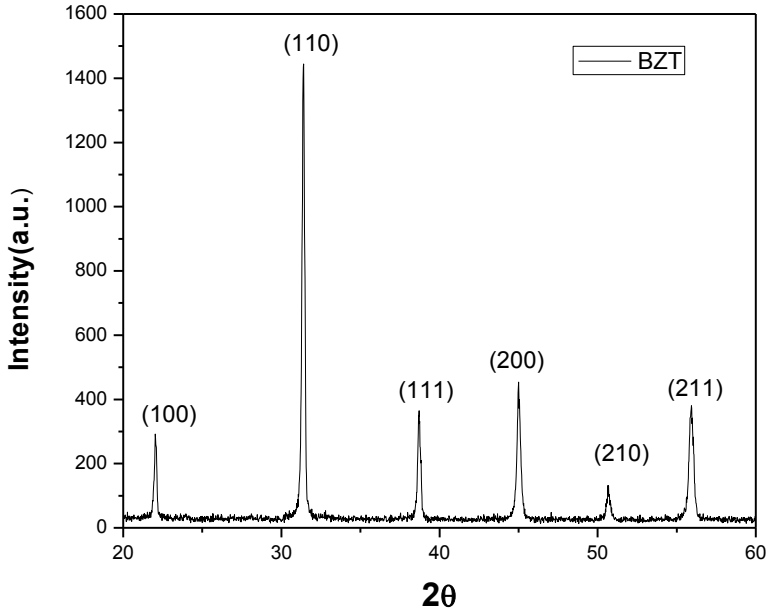


Fig.4 XRD of $BaZr_{0.1}Ti_{0.9}O_3$ ceramic

Fig4. shows the XRD pattern of BZT ceramic powder calcined at 1200^0 C for 6 hrs .The pattern shows the clear single perovskite phase without any secondary phase.

2. SEM

The figure above shows the surface morphology of the hot pressed 100% PVA and the polymer composite .The lighter region in the fig represents the ferroelectric ceramic and the darker region the polymer matrix. With the increase in the ceramic concentration the distribution becomes uniform.

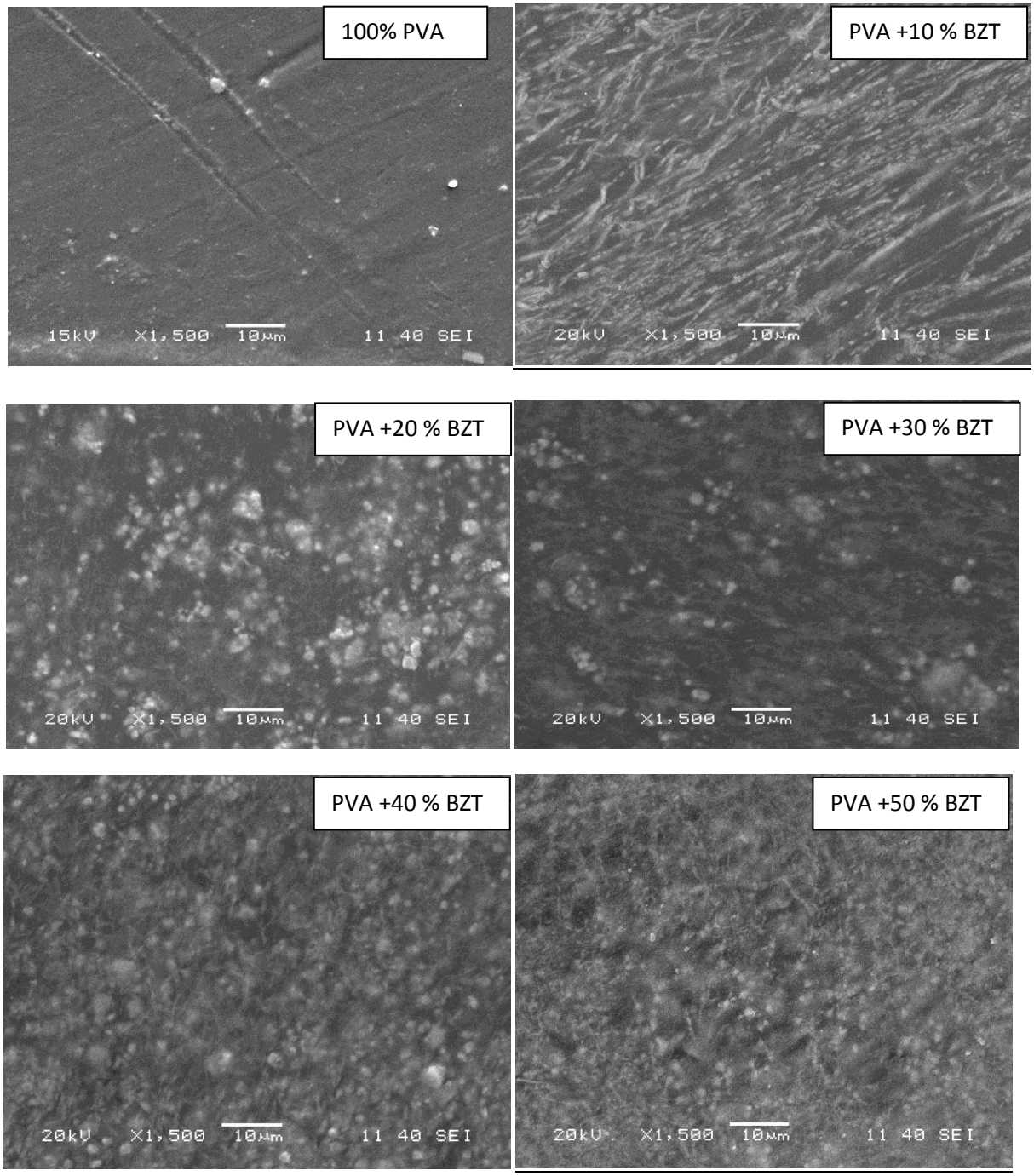


Fig.5 SEM Micrograph of hot pressed polymer composite

3. Dielectric study

Dielectric spectroscopy also known as electrochemical impedance spectroscopy measures the dielectric properties of medium as a function of frequency .It is based on the interaction of an external field with the electric dipole moment of the sample.

3.1. Frequency dependence dielectric study

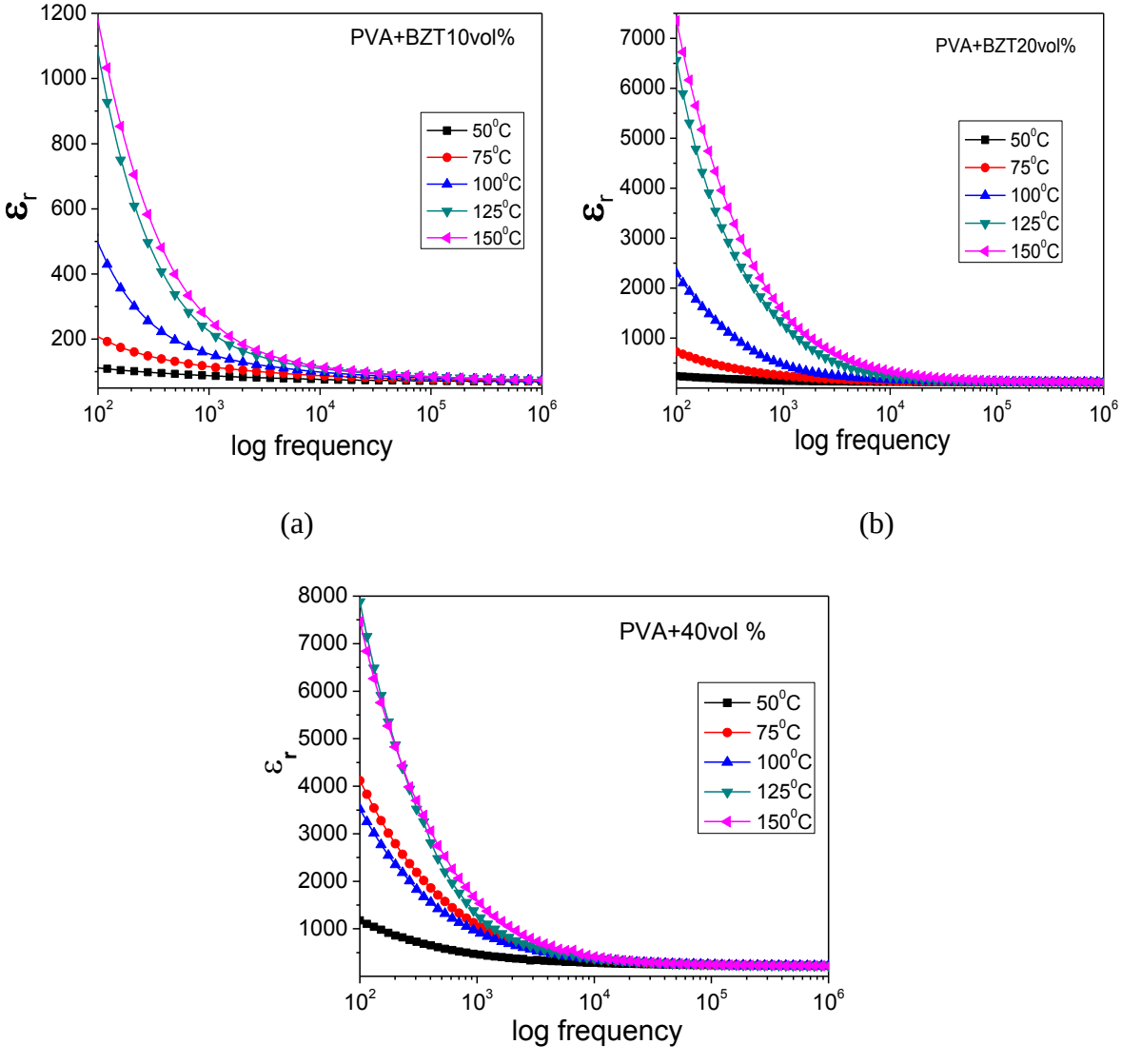


Fig.6 Frequency dependence of ε_r of polymer ceramic composite at various temperatures

For polymer ceramic composites, the perovskite-type ceramics is in the powder form instead of the sintered form. The removal of grain boundaries, elimination of constrained forces from neighboring grains and a drop in domain density due to decrease in the particle size will change the relaxation mechanisms of ceramic powders. Hence, sintered and unsintered ceramic powders show a different dielectric behavior. Our work deals with a composite medium composed of dispersed unsintered modified ceramic within the polymer matrix. Figure 6 shows the frequency dependence of dielectric constant at temperatures between 50 and 150 °C of the samples PVA+BZT10vol% (a) PVA+BZT20vol% (b), and PVA+BZT40vol% (c). A relatively high dielectric constant at low frequencies is a characteristic of polymer as well as oxide ceramic. So, the nature of the dielectric constant ε can be expressed as follows, dielectric constant ε can be expressed as follows,

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} \qquad (1)$$

Where ε_s and ε_∞ are the static and infinite dielectric constant values respectively, ω is the angular frequency and τ is the relaxation time. At very low frequencies *($\omega \ll 1/\tau$, τ=*relaxation time), dipoles follow the field and we have $\varepsilon_r = \varepsilon_s$ (value of the dielectric constant at quasistatic fields). As the frequency increases (with $\omega < 1/\tau$), dipoles begin to lag behind the field and ε slightly decreases. When frequency reaches the characteristic frequency ($\omega = 1/\tau$), the dielectric constant drops (relaxation process). At very high frequencies *($\omega \gg 1/\tau$)*, dipoles can no longer follow the field and $\varepsilon_r \approx \varepsilon_\infty$ (high-frequency value of ε_r). Qualitatively, the same behavior has been observed in Fig.6. At low temperatures, the ε value decreases monotonically with increasing frequency and attains a constant value at high frequencies. This behavior is typical of polar dielectrics/polymers because dipole orientation is facilitated by increasing the temperature, thus increasing the permittivity. The same nature is observed in all the composites, but the shift reduces with incorporating ceramics in polymer-ceramic composite.

3.2. Frequency dependence tangent loss

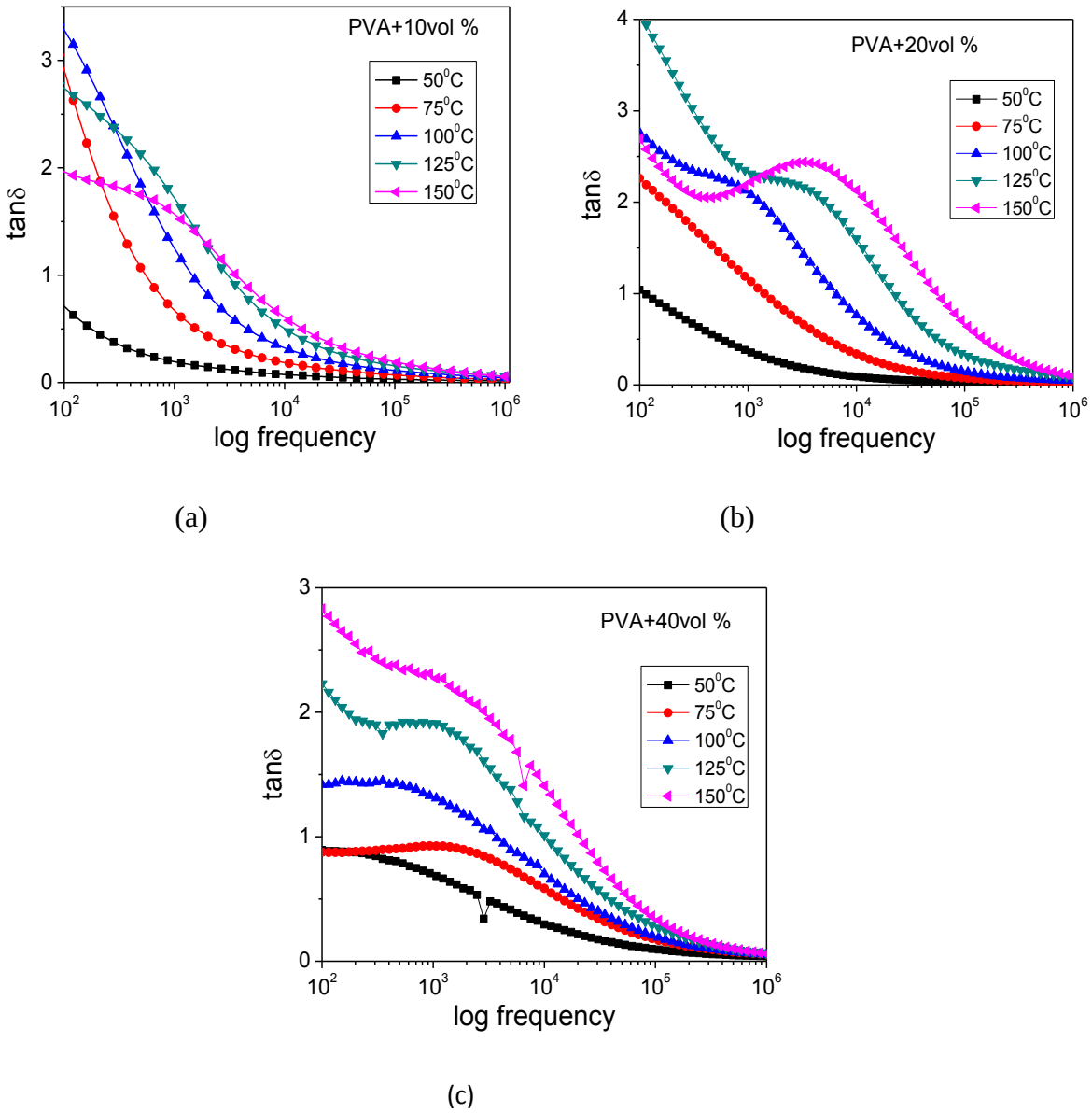


Fig. 7 Frequency dependence of tanδ of polymer ceramic composite at various temperatures

Figure 7 illustrates the variation of tangent loss for all composites at different temperatures as a function of frequency. In the amorphous phase, dipolar molecules can be able to orient from one equilibrium position to another relatively easily, and contribute to absorption over a wide frequency or temperature range [12,14]. In the present study, the high dielectric loss occurs at the lower frequency is due to accumulation of free charges at the interface between the electrolyte and the electrode (space charge polarization). At higher frequencies, the periodic

reversal of the electric field occurs so fast that there is no excess charge diffusion in the direction of the field. So, the charge accumulation decreases, leading to a decrease in the value of the dielectric loss. Then, the clear peak position appears above 150^{o}C in PVA+BZT10wt% (position increases with addition of ceramics) and shifts towards higher frequency side with increase in temperature. The loss peaks and their shifts with temperature suggest a thermally activated dielectric relaxation process [13].

3.3. Impedance spectroscopy

In the heterogeneous system (i.e., mixed state of polymer + ceramic), it is necessary to explain the impedance spectroscopy to understand the complete relaxation and conduction mechanism presence in the samples. In the polymer, segmental chains are involved in the relaxation process whereas in ceramic, dipoles are involved and the conductivity of two systems is different in nature. The complex impedance spectrum of the polymer composites at 100^{o}C is shown in Fig. 8. It can be clearly seen that the different kind of behavior is present in the spectrum; which confirms that the additional behavior added while increasing ceramic concentration in the polymer composites. At PVA+BZT10vol% shows the single relaxation behavior, as it contain small amount of ceramic (10vol%) (PVA dominates the ceramic-polymer interface effect), but in the PVA+BZT20vol% and PVA+BZT40vol% shows the additional effects. It may be due to the adding of ceramic powder into the polymer which creates the interface effect and the higher concentration (40vol%) space charge polarization added to the other effects. These kinds of nature can be explained in simple common model contains a serial arrangement of one, two and three units that represent the contribution from the bulk composite interface region and the space charge polarization of the ceramic–polymer composite respectively. Each unit is depicted by a parallel combination of two possible electrical current components, i.e., resistor and capacitor . The impedance datas are analyzed to an equivalent circuit consisting of different RC combination as mentioned above. The constant phase element (CPE) is introduced as the material obeys non-Debye type behavior which replaced the capacitance from the electrical equivalent circuit . The impedance of CPE is:

$$Z_{CPE} = [Q(j\omega)^{\alpha}]^{-1} \qquad (2)$$

where Q indicates the value of the capacitance of the CPE element and α the degree of deviation with respect to the value of the pure capacitor.

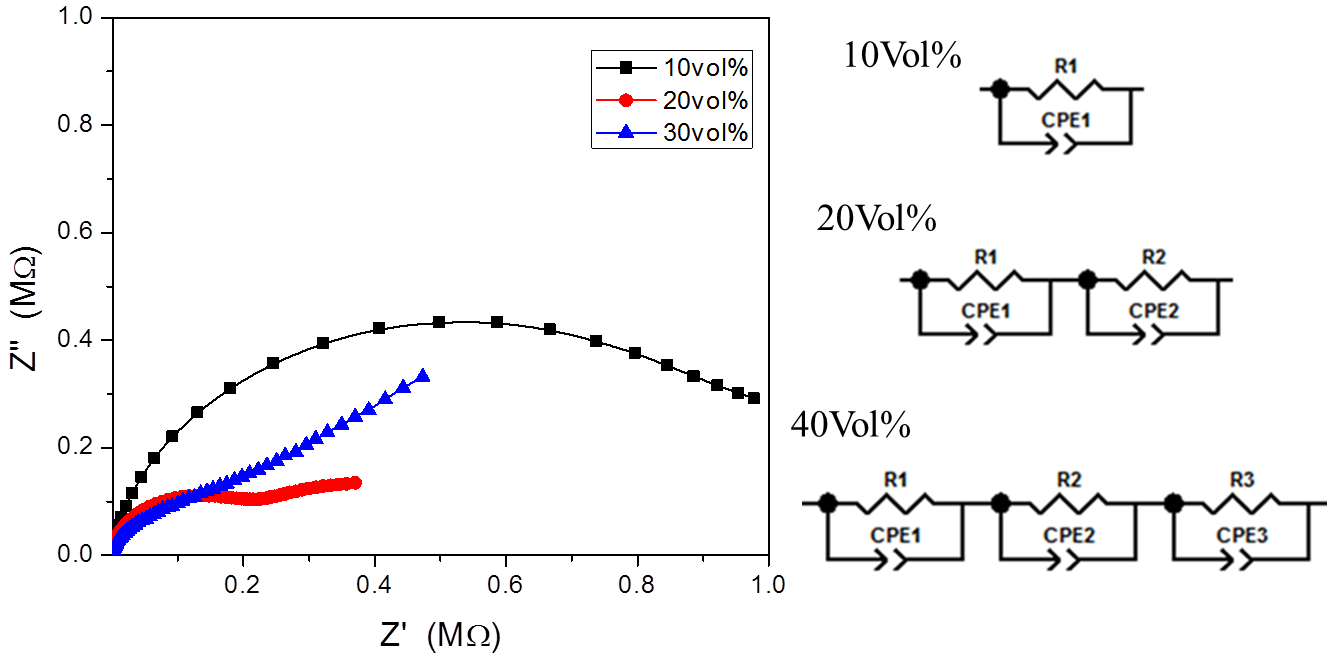


Fig. 8 Cole-Cole plot

3.4. Frequency dependence imaginary impedance

Figure 9 shows the variation of the imaginary part of impedance (Z'') with frequency at different temperature. The curves show that the Z" values reach a maxima peak (Z" max) and the value of Z" max shifts to higher frequencies with increasing temperature. A typical peak broadening, slightly asymmetrical in nature can be observed with the rise in temperature. The broadening of peaks in frequency explicit plots of Z" suggests that there is a spread of relaxation times, i.e. the existence of a temperature dependent electrical relaxation phenomenon in the material. The merger of Z" values in the high frequency region may possibly be an indication of the accumulation of space charge in the material. The relaxation process may be due to the presence of immobile species at low temperature and defects at higher temperature. In such a situation, one can determine the activation energy by the linear

fit of the temperature dependence of relaxation frequency, which satisfies the Arrhenius law as shown in the Fig.9 inset. The law is as follows;

$$f_{max} = f_o exp\left(\frac{E_a}{KT}\right) \qquad (3)$$

where, f_{max} is the maximum peak frequency, f_o is the characteristic frequency, K is the boltzmann constant, E_a is the activation energy for the migration of free charges and T is the absolute temperature. Activation energy increases with increasing the ceramic concentration in polymer composite, which indicates the hardening of polymer chain when the more ceramic particles incorporating into the polymer matrix.

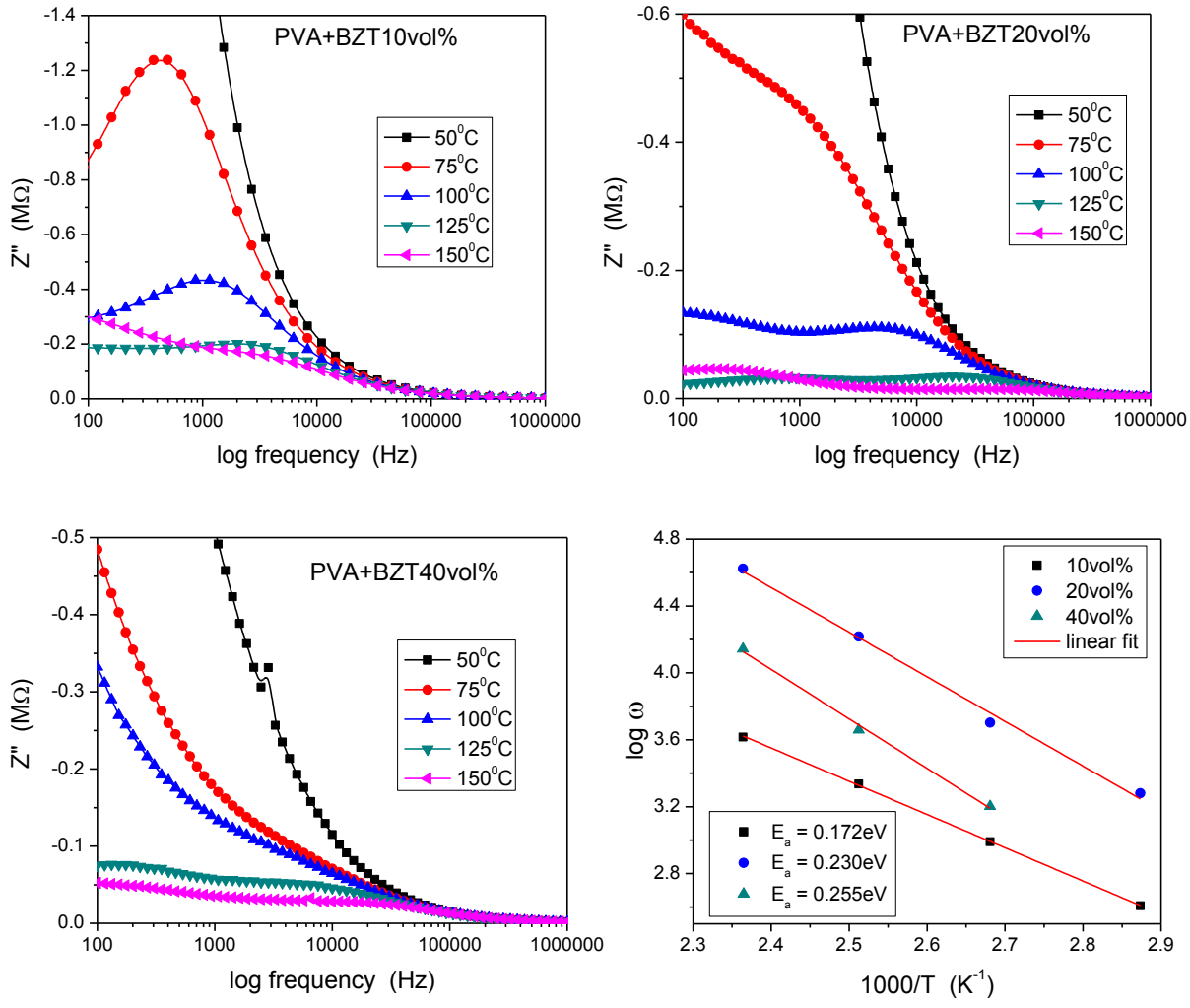


Fig. 9 Imaginary part of impedance vs frequency

1.1. AC conductivity study

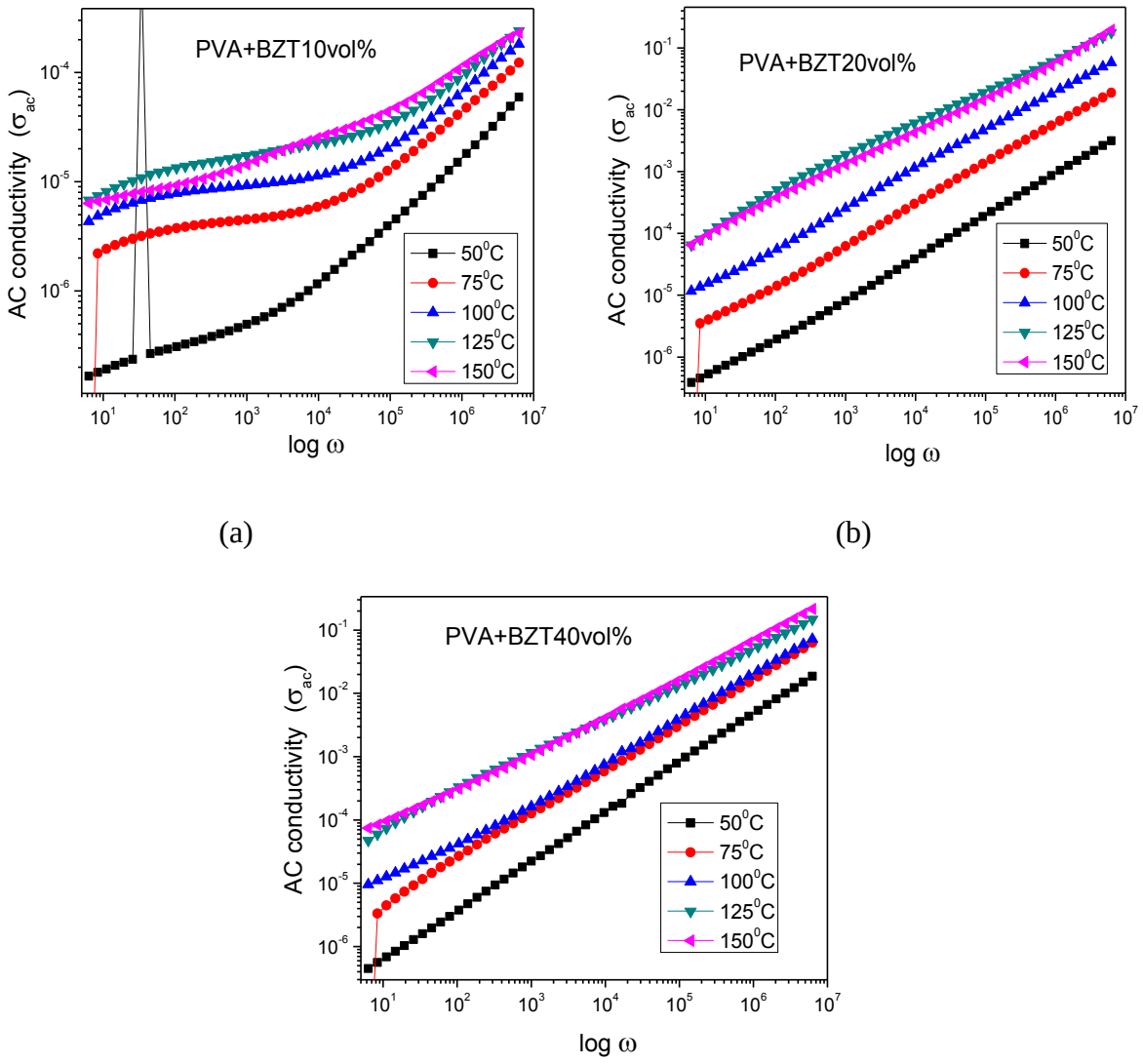


Fig. 10 AC conductivity vs angular frequency

AC conductivity has been studied as a function of frequency in the temperature range 50-150 °C for all the compositions and the typical plot of $\log\sigma_{ac}$ vs $\log\omega$ is shown in Fig. 10. The characteristic features of conductivity spectra can be explained using Jonscher's power law[24]; $\sigma_{ac} = \sigma_{dc} + A\omega^n$ $(0 < n < 1)$ where A is a temperature dependent pre-exponential factor and n is the power law exponent. The exponent n represents the degree of interaction between mobile ions and lattices. The factor A determines the strength of the polarizability of the sample. The conductivity of all the samples apparently enhanced with increasing

temperature. This can be easily understood based on the segmental chain motion of polymer composites. When the temperature is increased, mobility of polymer chains is enhanced, and the fraction of free volume in polymer composite increases accordingly, which leads to an increase in the conductivity of the pure polymer. Furthermore, the number of charge carrier increases with increasing temperature especially in modified ceramics due to the oxygen vacancies. This is favorable to a high conductivity at higher temperatures. The frequency independent behavior of the conductivity in the low frequency region is observed but that become sensitive at high frequency region, which generally known as hopping frequency, shifted towards the higher frequency side with an increase of temperature. The high-frequency conductivity dispersion may be attributed to AC conductivity whereas the frequency independent plateau region of the conductivity pattern corresponds to the dc conductivity (σ_{dc}) of the sample.

Conclusion

The ferroelectric ceramic $BaZr_{0.1}Ti_{0.9}O_3$ was prepared by solid state method. XRD pattern of the powder calcined at 1250 ^{0}C for 6 hr and the pattern shows clear single perovskite phase. SEM micrograph shows the homogeneous distribution of the ceramic in the polymer. With increasing ceramic composition the distribution becomes uniform. From the dielectric measurement various electrical properties were studied. We found that dielectric constant increased with the rise in frequency & rise in temp for a particular composition .It is also found that dielectric constant increased with the increase in the ceramic concentration. Dielectric loss also increased with increase in temp at lower frequency. As well it increased with increase in the ceramic composition. From impedance spectroscopy additional behavior is introduced with the increase in the ceramic composition. For a particular composition the Z'' decreases with increasing frequency and the peak shift towards higher frequency. Activation energy increased with the increase in the ceramic concentration implying the hardening of polymer chain. AC conductivity increased with the increase in the temp and also ceramic concentration.

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